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U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-CR-132

**IMPROVED FILTRATION MATERIALS AND MODELING
FINAL COMPREHENSIVE REPORT**

M. Douglas LeVan

UNIVERSITY OF VIRGINIA
Charlottesville, VA 22903-2442

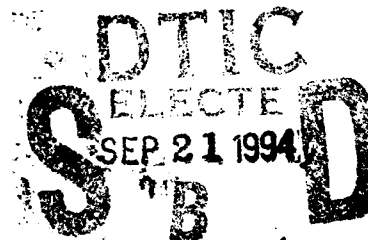
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PREFACE

The work described in this report was authorized under Contract No. DAAA15-90-C-0012, Task No. A002. This work was started in June 1990 and completed in June 1993.

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IMPROVED FILTRATION MATERIALS AND MODELING FINAL COMPREHENSIVE REPORT

INTRODUCTION

Adsorbents, usually impregnated activated carbons, are used in filters. Activated carbons, especially when dry, have a high capacity for organic vapors. This capacity decreases as polarity and volatility of the challenge increases. Thus, much of a contaminant is removed from air by the normal adsorption mechanism, i.e., physical adsorption. Chemical impregnants serve to help the process by destroying the contaminant by chemical reaction (catalytic mechanism) or permanently binding to the contaminant by chemical adsorption (non-catalytic mechanism), in which case the impregnant is effectively consumed and the adsorbent is non-regenerable.

Conditions of high humidity pose special problems for activated carbon filters. The extent of water adsorption on common activated carbons is small at conditions below 30 to 40% relative humidity. However, above 60% relative humidity, water adsorbs significantly. Under these conditions water competes with the contaminant for the adsorption space (surface area or pore volume). Rates can also be slowed significantly because the contaminant must diffuse in water-filled pores rather than in air-filled pores.

The two cyclic processes used for vapor phase processes are pressure swing adsorption and thermal swing adsorption. In pressure swing adsorption, feeds for different cycle steps are at different pressures but not different temperatures. In thermal swing adsorption, feeds for different cycle steps are at different temperatures and may also be at different pressures. The two cycles typically have one other important operating characteristic, that being that cycle steps in pressure swing adsorption are generally short (on the order of seconds to a few minutes) while in thermal swing adsorption they are generally long (on the order of many minutes to hours).

The purpose of the work carried out under this contract was to contribute to the development of a technical basis for reliable design of regenerable adsorption systems for the Army's special needs. The effort was carried out with frequent discussions with ERDEC personnel. Together with the concurrent research effort that occurred at ERDEC, considerable progress leading toward sound design methods was made as discussed below. Many factors were addressed such as the effect of water on adsorption equilibrium (which determines the ultimate capacity of a bed), the importance of various rate processes (which together with adsorption equilibrium determine the useful capacity of a bed), and the development of mathematical models for operation of beds in pressure swing cycles, with and without thermal effects.

The objective of this work was to develop new approaches to identify, measure, and correlate relevant data and derive appropriate mathematical models for designing and evaluating regenerable adsorbent-based air filtration systems. The contract contained two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria of vapors of organic compounds and water on BPL activated carbon, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. This final report discusses research accomplishments in the two areas and discusses the current status of knowledge in the areas.

The contract work proceeded as planned, was coordinated with ERDEC personnel at all times, and was consistent with the contract schedule. Research discussions were held between M. D. LeVan and ERDEC personnel at ERDEC or the University of Virginia at least once each quarter.

RESEARCH ACCOMPLISHMENTS

Research accomplishments are itemized below. The two areas, adsorption equilibrium and PSA modeling, are considered separately. *After each itemized accomplishment, reference is given to the quarterly report in which the work was described, a thesis or dissertation in which comprehensive details can be found, and any publication or presentation based on the work. Copies of all theses and dissertations were delivered to Dr. David E. Tevault when they were received from the binder. ERDEC has copies of all quarterly reports, presentations, and publications.*

Adsorption Equilibrium

The research involved the adsorption of water and other compounds on activated carbon. Our goals were to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. Our approach has been to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This permits more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

Discussions with ERDEC personnel helped to identify organic compounds for detailed study (see quarterly reports #4, 7, and 9). The discussions indicated that compounds should be chosen on the basis of volatility, water solubility, and molecular size.

Our research accomplishments in the adsorption equilibrium area were as follows:

- Water adsorption/desorption isotherms were measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased. [Quarterly reports: 1-3; Dissertation: Rudisill, 1991; Presentation: LeVan, 1991; Publication: Rudisill et al., 1992]
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C,

50°C, 75°C, and 100°C from low pressures to saturation. We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We did this by performing an experiment with CFC-113 at 50°C. [Quarterly reports: 5-7; Thesis: Eissmann, 1992; Presentations: Eissmann and LeVan, 1992; Publication: Eissmann and LeVan, 1993]

- Adsorption/desorption isotherms for n-hexane/water, acetone/water, and CFC-113/water coadsorption on BPL activated carbon were measured at 25°C and 100°C. (Prior to the start of the contract we had measured pure component isotherms for hexane and acetone on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C.) Isotherms for dichloromethane/water were measured at 25°C; attempts to measure similar isotherms at 100°C showed that dichloromethane was very reactive in our apparatus at this temperature with water present. Our data show the following:
 - The hysteresis loops for water were found to persist with coadsorption of the hydrocarbon or halocarbon and closed with increasing temperature.
 - The presence of adsorbed water was found to increase the partial pressure of the adsorbed organic compound, with the extent of this increase depending on the system and being more pronounced for n-hexane/water than acetone/water.
 - Data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicate a very strong dependence of quantity of water adsorbed on water solubility in the organic compound.

[Quarterly reports: 3-7; Dissertation: Rudisill, 1991; Thesis: Eissmann, 1992; Presentations: LeVan, 1991, Eissmann and LeVan, 1992; Publications: Rudisill et al., 1992, Eissmann and LeVan, 1993]

- We modified and calibrated our adsorption equilibrium apparatus to measure adsorption equilibrium for coadsorption of light gases and water. This required a major change of the injection system of the apparatus. [Quarterly reports: 8,9]
- Adsorption isotherms of propane on BPL carbon were measured from low pressure to several atmospheres at 25°C, 50°C, 75°C, 100°C, and 125°C. Limited data were measured for the system propane/water. [Quarterly report: 10]

- We ran tests to confirm that nitrogen carrier gas at 0.1 MPa does not compete to any measurably degree with propane for the adsorption space in BPL carbon. These tests were performed by substituting helium for nitrogen. No differences in propane loading as a function of propane pressures were found. Later, we remeasured pure component isotherms of propane adsorbed on BPL carbon at 25°C and 100°C. The data were measured with helium in the recirculation loop although, based on the results, we could just as well have used nitrogen. [Quarterly reports: 10-12]
- We set up our adsorption equilibrium apparatus and began measurement of organic/water adsorption equilibrium for n-octane and water coadsorbed on BPL activated carbon. [Quarterly report: 12]
- We determined isosteric heats of adsorption directly from our data for the components on which we have comprehensive adsorption equilibrium data. The behavior of isosteric heat of adsorption with loading gives us qualitative information on heterogeneity of the adsorbent and adsorption mechanism. [Quarterly reports: 9, 10; Thesis: Russell, 1993]
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are based on correct physical structure (to the extent possible). [Quarterly report: 7; Thesis: Russell, 1993]
- We measured nitrogen adsorption and desorption isotherms on our BPL carbon using a BET apparatus in our laboratory. This contributes to our understanding of BPL carbon. [Quarterly report: 9; Thesis: Russell, 1993]
- We applied mean-field density-functional theory to determine the pore size distribution of BPL activated carbon using a nitrogen isotherm at 77 K that we measured. This method gave an alternative pore size distribution to that obtained using the Kelvin equation and water desorption isotherms measured under the contract. [Quarterly report: 10; Thesis: Russell, 1993]
- We began a detailed, comprehensive study of the pore size distribution of BPL activated carbon. It is our belief that further development and improvements of physical models for adsorption equilibria will require a thorough understanding of the pore size distribution. We are applying all popular methods based on nitrogen adsorption and water desorption to data that we have measured. [Quarterly report: 12]

- We developed correlations and interpretations of the data on BPL carbon for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We have pursued several related approaches, ranging from largely physical interpretations to purely mathematical descriptions. Some of these are described in the items below. [Quarterly reports: 7-12; Theses: Eissmann, 1992, Russell, 1993]
- We began the development of methods that we believe should guarantee the accurate correlation of adsorption equilibrium data over the range of the data. The methods are based on the use of series expansions in terms of polynomials that are orthogonal to summation, although non-orthogonal polynomials could also be used. In implementing the method, a multicomponent, temperature-dependent virial-type equation arises naturally. [Quarterly reports: 10-12]
- We completed the initial development of a semi-empirical model to describe the adsorption of pure gases and vapors in microporous adsorbents in general, and the adsorption of water vapor and pure organic compounds on BPL activated carbon in particular. The model assumes that the adsorbate molecules are localized on the adsorbent surface. Allowance is made for multilayer formation and pore filling as the pressure is increased. The heterogeneity of the adsorbent surface and lateral interactions among adsorbate molecules are also accounted for in a simple fashion. [Quarterly reports: 10-12; Thesis: Russell, 1993]
- We extended the pure component isotherm equations referred to immediately above to adsorption of mixed vapors of organic compounds and water. Our isotherm equations predict experimental adsorption isotherms reasonably well for much of our organic/water data, but we have found that much better agreement can be obtained by introducing a binary adsorbate-adsorbate interaction parameter. [Quarterly reports: 10-12; Thesis: Russell, 1993]
- We designed a new apparatus to measure pure gas isotherms for light organic compounds and their mixtures with water vapor. We believe that the apparatus will give improved performance over our existing apparatus when applied to light adsorbates. The apparatus is housed in an environmental chamber and can be operated in two different modes. First, for measurement of pure isotherms, gas is injected into a closed loop using a gas injection system and is recirculated until equilibrium is established,

as determined and measured with a gas chromatograph. Second, for measurement of mixture isotherms of the organic compound and water, the apparatus is initially used in a flow-through mode to saturate the adsorbent at a chosen relative humidity. This is a major change from our existing apparatus, which attempts to fix adsorbed rather than vapor concentrations. During the flow-through step, the environmental chamber is slowly cooled or heated to put the components on an adsorption or desorption branch of the isotherm. After the bed is saturated as desired, the apparatus is reconfigured in a closed loop and heated with circulation to remove the adsorbates, which are collected in a liquid nitrogen trap for later analysis by pressure and gas chromatograph measurements after expansion back to vapor. [Quarterly report: 10]

PSA Modeling

We have constructed robust, generic mathematical models for PSA. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL. [Quarterly reports: 1-3; Thesis: King, 1991]
- We have constructed fixed-bed *rate* models and studied their behavior for a wide range of operating conditions. The models are based on explicit equation sets ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. This was done to reduce the computer time necessary to run the model. Some details are as follows.
 - We have included both intraparticle diffusion and convection effects in the rate

models. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps, such as those used with weakly adsorbed light gases.

- As part of the development of these models, we discovered a significant simplification in the way to write and solve rate models for isothermal PSA (and, approximately, for non-isothermal PSA). Previous models in which bed pressure was allowed to vary in time but not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed: this is done by integrating the balance over the length of the bed (see quarterly report #7).

[Quarterly reports: 3-10; Thesis: Vishnoi, 1992]

- M. D. LeVan developed PSA simulation models (isothermal and non-isothermal) and dispersion models to analyze data gathered at ERDEC. The PSA models use the newly discovered way of treating the dP/dt derivative mentioned above. Thus, pressurization and blowdown steps are treated by these models. Tests of these models have been conducted at ERDEC. John J. Mahle modified the non-isothermal PSA model to try to predict the large temperature changes found in the PSA experiments for CFC-113. [Quarterly reports: 7-10]

- A computer program for a new type of dispersion model, using mixing cells with bypasses, was developed by M. D. LeVan following discussions with Dr. David K. Friday. Near the end of the contract, we continued to develop this model in collaboration with John J. Mahle to analyze PSA data gathered at ERDEC. [Quarterly reports: 9-12]

PRESENTATIONS AND PUBLICATIONS

Refereed Publications:

- Rudisill, E. N., Hacskeylo, J. J., and LeVan, M. D., "Coadsorption of Hydrocarbons and Water on BPL Activated Carbon," *Ind. Eng. Chem. Research*, **31**, 1122-1130 (1992).
- Friday, D. K., LeVan, M. D., Mahle, J. J., and Buettner, L. C., "PSA for Air Purification: Experiments and Modeling," in Suzuki, M. (ed.), *Fundamentals of Adsorption*, in press (1993).
- Eissmann, R. N., and LeVan, M. D., "Coadsorption of Organic Compounds and Water Vapor on BPL Activated Carbon. II. 1,1,2-Trichloro-1,2,2-trifluoroethane and Dichloromethane," *Ind. Eng. Chem. Research*, in press (1993).

Conference Presentations:

- LeVan, M. D., Plenary Lecture, "Factors in the Performance of Regenerable Filters," 1990 U. S. Army CRDEC Scientific Conference, Aberdeen Proving Ground, Maryland, November 1990; published in the conference proceedings.
- LeVan, M. D., "Multicomponent Adsorption Equilibria for Vapors of Hydrocarbons and Water on Activated Carbon," 1991 U. S. Army CRDEC Scientific Conference, Aberdeen Proving Ground, Maryland, November 1991; published in the conference proceedings.
- Friday, D. K., LeVan, M. D., Mahle, J. J., and Buettner, L. C., "Pressure Swing Adsorption for Air Purification: Experiments and Modeling," Fourth International Conference on Fundamentals of Adsorption, Kyoto, Japan, May 1992.
- Eissmann, R. N., and LeVan, M. D., "Vapor-Phase Adsorption Equilibria of Halocarbon - Water Mixtures on Activated Carbon," Symposium on Recent Advances in Adsorption, AIChE 1992 Annual Meeting, Miami Beach, Florida, November 1992.
- Eissmann, R. N., and LeVan, M. D., "Vapor-Phase Adsorption Equilibria of Halocarbon - Water Mixtures on Activated Carbon," 1992 U. S. Army ERDEC Scientific Conference, Aberdeen Proving Ground, Maryland, November 1992; published in the conference proceedings.

Additional presentation: STAS for Assessing the Modeling of Pressure Swing Adsorption Technology, Aberdeen Proving Ground, Maryland, October 1990.

Dissertations and Theses:

Rudisill, E. N., "Studies on Water-Hydrocarbon Adsorption Equilibria and Adsorptive and Membrane Separations," Ph.D. dissertation, May 1991.

King, R., "Simulation of the Pressure Swing Adsorption Process," M.S. thesis, May 1991.

Eissmann, R. N., "Vapor-Phase Adsorption Equilibria of Halocarbon/Water Mixtures on Activated Carbon," M.S. thesis, May 1992.

Vishnoi, A., "Role of Intraparticle Convection in Pressure Swing Adsorption Processes," M.S. thesis, August 1992.

Russell, B. P., "Adsorption of Gases in Porous Carbons," M.S. thesis, May 1993.

Croft, D., Ph.D dissertation, in progress.

Taqvi, S. M., Ph.D. dissertation, in progress.

Russell, B. P., Ph.D. dissertation, in progress.

Dunne, K. I., M.S. thesis, in progress.

CURRENT STATUS AND CONCLUDING REMARKS

The research in this contract complemented that occurring at ERDEC. Initial development of mathematical models for PSA was done by M. D. LeVan, building on research carried out by graduate students at the University of Virginia. *These models were then delivered to ERDEC where they were used to predict results of PSA experiments.* Models were modified by J. J. Mahle and M. D. LeVan to give reasonable prediction of experimental results. Two main models were developed. The first, an orthogonal collocation based model, provided the early basis for predictions (see the referenced publication by Friday, LeVan, Mahle and Buettner, 1993). This model was innovative in that it included the determination of the rate of change of pressure in the bed as a whole as described above in the section on Research Accomplishments (PSA Modeling). While this model provided reasonable predictions, it was felt that it was inadequate in predicting low concentrations and did not characterize axial dispersion properly. So, M. D. LeVan constructed a second model based on mixing cells with bypasses. The ability to treat pressure changes in the bed as a whole was included in this model also. The model was developed further by J. J. Mahle, who added an energy balance and other extensive changes, and M. D. LeVan, who made refinements including changes to make the code run faster. This model is felt to work quite well. It provides the current basis for analyzing data from PSA experiments at ERDEC.

In the area of adsorption equilibrium, measurements were made for organic compounds, water, and organic/water mixtures adsorbed on BPL activated carbon. Considerable understanding was gained on the behavior of these systems. Progress was made in the development of correlative approaches and predictive methods for adsorption equilibrium. Additional data will be needed for systems of light organic compounds and water to have a comprehensive understanding of adsorption of organic/water mixtures on activated carbon.

Under a new contract, further measurements of adsorption equilibrium are occurring using a new apparatus designed for light organics and water. The development of correlative and predictive methods for adsorption equilibrium is continuing. Additional development of the PSA model and models for thermal swing adsorption is also being pursued.

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APPENDIX A: Final Quarterly Report
Quarterly Report #12

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Period Covered: March 13, 1993 – June 12, 1993

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals have been to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We have determined the effects of water vapor on the adsorption of vapors of organic compounds. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach has been to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This permits more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms were measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation. We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We did

this by performing an experiment with CFC-113 at 50°C.

- Adsorption/desorption isotherms for n-hexane/water, acetone/water, and CFC-113/water coadsorbed on BPL activated carbon were measured at 25°C and 100°C. (Prior to the start of the contract we had measured pure component isotherms for hexane and acetone on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C.) Isotherms for dichloromethane/water were measured at 25°C; attempts to measure similar isotherms at 100°C showed that dichloromethane was very reactive in our apparatus at this temperature with water present. Our data show the following:
 - The hysteresis loops for water were found to persist with coadsorption of the hydrocarbon or halocarbon and closed with increasing temperature.
 - The presence of adsorbed water was found to increase the partial pressure of the adsorbed organic compound, with the extent of this increase depending on the system and being more pronounced for n-hexane/water than acetone/water.
 - We have found that data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicates a very strong dependence of quantity of water adsorbed on water solubility in the organic compound.
- Adsorption isotherms of propane on BPL carbon were measured from low pressure to several atmospheres at 25°C, 50°C, 75°C, 100°C, and 125°C. Limited data were measured for the system propane/water.
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are based on correct physical structure (to the extent possible).
- Additional compounds have been identified for further, detailed study through discussions with ERDEC personnel. These are contained in previous quarterly reports. The discussions have indicated compounds should be chosen on the basis of volatility, water solubility, and molecular size. Discussions at ERDEC (January, 1992) have indicated the need to consider some lighter gases coadsorbed with water. In other discussions (June, 1992), propane, either ethane or n-butane, and CFC-12 were identified for study. Also, studies of coadsorption of mixed organic vapors of compounds differing greatly in volatility has been suggested; these have not been studied to any significant degree and should be both interesting and a challenging test for predictive models.

- We modified and calibrated our adsorption equilibrium apparatus to measure adsorption equilibrium for coadsorption of light gases and water. This is a major change of the injection system of the apparatus.
- We measured nitrogen adsorption and desorption isotherms on our BPL carbon using a BET apparatus in our laboratory. This contributes to our understanding of BPL carbon.
- We ran tests to confirm that nitrogen carrier gas at 0.1 MPa does not compete to any measurably degree with propane for the adsorption space in BPL carbon. These tests were performed by substituting helium for nitrogen. No differences in propane loading as a function of propane pressures were found. Later, we remeasured pure component isotherms of propane adsorbed on BPL carbon at 25°C and 100°C. The data were measured with helium in the recirculation loop although, based on the results, we could just as well have used nitrogen [12].
- We determined isosteric heats of adsorption directly from our data for the components on which we have comprehensive adsorption equilibrium data. The behavior of isosteric heat of adsorption with loading gives us qualitative information on heterogeneity of the adsorbent and adsorption mechanism.
- We have applied mean-field density-functional theory to determine the pore size distribution of BPL activated carbon using a nitrogen isotherm at 78 K that we measured. This method gave a pore size distribution that agreed remarkably well with the pore size distribution that we obtained using the Kelvin equation and water desorption isotherms measured previously by Rudisill under the contract. This is a confirmation of nanometer scale structural information for BPL activated carbon.
- We have developed correlations and interpretations of the data on BPL carbon for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We have pursued several related approaches, ranging from largely physical interpretations to purely mathematical descriptions.
- We have developed methods that we believe should guarantee the accurate correlation of adsorption equilibrium data over the range of the data. The methods are based on the use of series expansions in terms of polynomials that are orthogonal to summation,

although non-orthogonal polynomials could also be used. In implementing the method, a multicomponent, temperature-dependent virial-type equation arises naturally.

- We have completed the initial development of a semi-empirical model to describe the adsorption of pure gases and vapors in microporous adsorbents in general, and the adsorption of water vapor and pure organic compounds on BPL activated carbon in particular. The model assumes that the adsorbate molecules are localized on the adsorbent surface. Allowance is made for multilayer formation and pore filling as the pressure is increased. The heterogeneity of the adsorbent surface and lateral interactions among adsorbate molecules are also accounted for in a simple fashion.
- We have extended the pure component isotherm equations referred to immediately above to adsorption of mixed vapors of organic compounds and water. Our isotherm equations predict experimental adsorption isotherms reasonably well for much of our organic/water data, but we have found that much better agreement can be obtained by introducing a binary adsorbate-adsorbate interaction parameter.
- We designed a new apparatus to measure pure gas isotherms for light organic compounds and their mixtures with water vapor. The apparatus is described in detail in a proposal submitted to ERDEC. We believe that the apparatus will give improved performance over our existing apparatus when applied to light adsorbates. The apparatus is housed in an environmental chamber and can be operated in two different modes. First, for measurement of pure isotherms, gas is injected into a closed loop using a gas injection system and is recirculated until equilibrium is established, as determined and measured with a gas chromatograph. Second, for measurement of mixture isotherms of the organic compound and water, the apparatus is initially used in a flow-through mode to saturate the adsorbent at a chosen relative humidity. This is a major change from our existing apparatus, which attempts to fix adsorbed rather than vapor concentrations. During the flow-through step, the environmental chamber is slowly cooled or heated to put the components on an adsorption or desorption branch of the isotherm. After the bed is saturated as desired, the apparatus is reconfigured in a closed loop and heated with circulation to remove the adsorbates, which are collected in a liquid nitrogen trap for later analysis by pressure and gas chromatograph measurements after expansion back to vapor.

During the present reporting period we accomplished the following:

- We set up our adsorption equilibrium apparatus and began measurement of organic/water adsorption equilibrium for n-octane and water coadsorbed on BPL activated carbon.
- We began a detailed study of the pore size distribution of BPL activated carbon. It is our belief that further development and improvements of physical models for adsorption equilibria will require a thorough understanding of the pore size distribution. We are applying all popular methods based on nitrogen adsorption and water desorption to such data that we have measured.
- We continued our development of correlations and interpretations of the data on BPL carbon for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water.
- We continued our development of methods, based on the use of series expansions in terms of polynomials that are orthogonal to summation, that we believe should guarantee the accurate correlation of adsorption equilibrium data.
- We continued the development of semi-empirical models to describe the adsorption of pure gases, water vapor, and mixtures of water vapor and organic compounds in microporous adsorbents in general and BPL activated carbon in particular.
- We continued to discuss the complementary and collaborative efforts occurring at ERDEC and the University of Virginia on measurement, interpretation, and correlation of adsorption equilibrium.

PSA Model

We have constructed robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of

the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.

- We have constructed fixed-bed *rate* models and studied their behavior for a wide range of operating conditions. The models are based on explicit equation sets ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. This was done to reduce the computer time necessary to run the model.
 - We have included both intraparticle diffusion and convection effects in the rate models. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps, such as those used with weakly adsorbed light gases.
 - As part of the development of these models, we discovered a significant simplification in the way to write and solve rate models for isothermal PSA (and, approximately, for non-isothermal PSA). Previous models in which bed pressure was allowed to vary in time but not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed; this is done by integrating the balance over the length of the bed.
- In work related to the contract, M. D. LeVan has developed PSA simulation models (isothermal and non-isothermal) and dispersion models to analyze data gathered at ERDEC. The PSA models use the newly discovered way of treating the dP/dt derivative mentioned above. Thus, pressurization and blowdown steps are treated by these models. Tests of these models have been conducted at ERDEC and continued development is occurring jointly. John J. Mahle has modified the non-isothermal PSA model to try to predict the large temperature changes found in the PSA experiments for CFC-113.
- Also, in work related to the contract, a computer program for a new type of dispersion

model was developed by M. D. LeVan following discussions with Dr. David K. Friday.

During the present reporting period we accomplished the following:

- We continued the development of our fixed bed rate models with and without intra-particle convection.
- In conjunction with John Mahle, we continued to collaborate on the development of a reliable PSA model to analyze data gathered at ERDEC.
- We continued to discuss the complementary and collaborative modeling efforts occurring at ERDEC and the University of Virginia on fixed bed modeling.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited ERDEC on March 25 and 26, 1993 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

This is the final quarter of the contract. The contract work proceeded as planned, was coordinated with ERDEC personnel at all times, and was consistent with the contract schedule.

N. Plans for activities during the following reporting period.

This is the final quarter of the contract. Research is continuing under a new contract with ERDEC.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

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APPENDIX B: Previous Quarterly Reports
Quarterly Report #1

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: September 28, 1990

Period Covered: June 13, 1990 – September 12, 1990

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our first goal is to establish a comprehensive understanding of water adsorbed by itself on activated carbon. Following this, we will consider the adsorption of other components separately and in combination with water.

Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. We are measuring water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During this reporting period, we measured water adsorption/desorption isotherms on Calgon Type BPL activated carbon at 75°C and 125°C for water pressures from low values to saturation. We also began preparations for modifying our apparatus to make measurements at lower temperatures.

PSA Model

This reporting period, we began the construction of our robust, generic mathematical model for PSA. We are beginning with the construction of an equilibrium model, to which we will later add mass and heat transfer resistances. We wrote computer code to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were coupled with an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. Four different boundary conditions were implemented for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The

balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL. Tests were run on the model to demonstrate that the model gives proper behavior for pressurization and depressurization for all combinations of boundary conditions.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC, Edgewood on July 5, 1990 and on August 6-7, 1990 for discussions on the research.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

First, we intend to measure water adsorption/desorption isotherms at 100°C for water pressures from low values to saturation. Then, we intend to modify our apparatus and measure water adsorption/desorption isotherms at 50°C, 25°C, and possibly 0°C.

PSA Model

During the next reporting period we will add an energy balance to our model. We will then compare predictions of the model with results in the literature using appropriate adsorption equilibrium relations.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Quarterly Report #2

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: January 10, 1991

Period Covered: September 13, 1990 – December 12, 1990

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our first goal is to establish a comprehensive understanding of water adsorbed by itself on activated carbon. Following this, we will consider the adsorption of other components separately and in combination with water.

Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the co-adsorption of other compounds. We are measuring water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the previous reporting period, we measured water adsorption/desorption isotherms on Calgon Type BPL activated carbon at 75°C and 125°C for water pressures from low values to saturation.

This reporting period, we accomplished the following:

- Measured water adsorption/desorption isotherms at 100°C
- Identified and eliminated two problems associated with the measurement of water isotherms at low temperatures with our apparatus. First, a black powder found in the closed loop of our apparatus and on which some water adsorption occurred was determined to be filings of stainless steel caused by abrasion in a magnetic recirculating pump. This had originally been thought to be dust from activated carbon. Switching to a new magnetic recirculating pump eliminated the problem. Second, our sampling system caused some water condensate to develop in the loop near, but somewhat

below, saturation of the gas phase. This was caused by mild pressure fluctuations that occurred during the pumping stroke and by a restriction in the loop to force gas through a gas sampling valve. This problem was eliminated by reducing the extent of the restriction in the loop.

- Began measuring water adsorption/desorption isotherms at lower temperatures. (As of the date of this report, isotherms at 50°C have been measured and the measurement of isotherms at 25°C is in progress.)
- Began the construction of a second adsorption equilibrium apparatus based on the same principles as our existing apparatus but using a metal bellows pump (Parker) rather than the reciprocating, long-stroke pump (Ruska).
- Developed theory to permit the simple extraction of spreading pressures from multi-component data measured with our apparatus. This determination of spreading pressures is necessary if activity coefficients are to be determined for nonideal adsorbed mixtures.

PSA Model

We have begun the construction of a robust, generic mathematical model for PSA as described in our previous quarterly report. Initially, we are constructing an equilibrium model, to which we will later add mass and heat transfer resistances. We have written computer code to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were coupled with an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. Four different boundary conditions were implemented for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL. Tests were run on the model to demonstrate that the model gives proper behavior for pressurization and depressurization for all combinations of boundary conditions.

This reporting period we accomplished the following:

- Added an energy balance to our model. This is done in a way similar to the implementation of a material balance – by adding a differential equation and boundary conditions to the equation set. The material balances and energy balances are cou-

pled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption.

- Began testing the model using results of Cheng and Hill (AIChE Journal, 1985) for methane adsorption from inert gas (helium) onto activated carbon. These results pertain to a novel three step cycle (pressurization, feed, and countercurrent blowdown [note - no purge step]). The cycle gives an interesting test of the model, although some questions concerning long-term operability of the cycle can be raised.

C. Results, positive or negative, obtained related to previously identified problem areas. with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on September 20 - 21 (research discussions), October 9 - 10 (research discussions and STAS panel [where presentations were made]), and November 15 - 16 (research discussions and 1990 Army CRDEC Scientific Conference [where a plenary lecture was given]).

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

First, we intend to complete our measurements of adsorption/desorption isotherms for water adsorbed on BPL activated carbon. We must complete our measurements at 25°C and resolve inconsistencies, if any exist, in all of the data as a whole. (We may also attempt to measure adsorption/desorption isotherms at 0°C.)

Second, we will begin to study in detail the co-adsorption of hydrocarbons and water vapor on BPL activated carbon. We intend to determine the effects of water vapor on adsorption of hydrocarbon vapors and, simultaneously, determine the effects of hydrocarbon vapors on the adsorption of water vapor. We have a considerable amount of pure component isotherm data for hexane and acetone adsorbed on BPL activated carbon. So, we anticipate starting with these hydrocarbons for our binary studies. Hexane is essentially immiscible with water while acetone is completely miscible.

PSA Model

During the next reporting period we will continue to test our mathematical model for pressure swing adsorption. Comparisons can be made between predictions of the model and experimental results – both published results and results obtained at CRDEC. For a true test, it is necessary to have appropriate adsorption equilibrium relations and physical and thermodynamic parameters. Also, in the near future, we will add rate equations to our model.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Blank

Quarterly Report #3

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: March 13, 1991

Period Covered: December 13, 1990 – March 12, 1991

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our first goal is to establish a comprehensive understanding of water adsorbed by itself on activated carbon. Following this, we will consider the adsorption of other components separately and in combination with water.

Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the co-adsorption of other compounds. We are measuring water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

We intend to determine the effects of water vapor on adsorption of hydrocarbon vapors and, simultaneously, determine the effects of hydrocarbon vapors on the adsorption of water vapor. Our first two hydrocarbons chosen for study are n-hexane and acetone. We have a considerable amount of pure component isotherm data on these substances. Hexane is essentially immiscible with water while acetone is completely miscible.

During the previous two reporting periods, we measured water adsorption/desorption isotherms on Calgon Type BPL activated carbon at 75°C, 100°C, and 125°C for water pressures from low values to saturation.

This reporting period, we accomplished the following:

- Measured water adsorption/desorption isotherms on BPL activated carbon at 25°C and 50°C for water pressures from low values to saturation.
- Measured adsorption/desorption isotherms for water and n-hexane coadsorbed on BPL

activated carbon at 25°C. The hysteresis loop for water was found to persist.

- Measured adsorption/desorption isotherms for water and acetone coadsorbed on BPL activated carbon at 25°C. The hysteresis loop for water was found to persist.
- Continued the construction of a second adsorption equilibrium apparatus. It is based on the same principles as our existing apparatus but using a metal bellows pump (Parker) rather than the reciprocating, long-stroke pump (Ruska).

PSA Model

We have begun the construction of a robust, generic mathematical model for PSA as described in our previous quarterly reports. Initially, we are constructing an equilibrium model, to which we will later add mass and heat transfer resistances. We have written computer code to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL. Tests were run on the model to demonstrate that the model gives proper behavior for pressurization and depressurization for all combinations of boundary conditions.

This reporting period we accomplished the following:

- Completed the first phase of the modeling effort. This work is described in detail in the Masters of Science thesis "Simulation of the Pressure Swing Adsorption Process" by Ronald K. King. The thesis was defended March 8, 1991. A copy of the thesis is being delivered to Dr. David Tevault with this report. Included in the thesis are tests of the model on the experimental system of Cheng and Hill (AIChE Journal, 1985) for methane adsorbed from inert gas (helium) onto activated carbon in a novel three-step PSA cycle. This cycle gives an interesting test of the model, although the question is raised by King of whether or not Cheng and Hill actually reached the periodic state (cyclic steady state).

- Began the development of our fixed-bed rate model for PSA. Our current thoughts are to develop a comprehensive model based on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) of King. Our purpose in doing so is to reduce the computer time necessary to run the model.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on December 17 - 18 and January 29 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- Measure equilibria for vapors of n-hexane and water and acetone and water coadsorbed on BPL activated carbon at 100°C.
- Begin work with hexanol, which is partially miscible with water. Both pure component adsorption and coadsorption with water vapor must be considered.
- Plan future work with lighter hydrocarbons.

PSA Model

- Continue our recently initiated work on a fixed-bed rate model for PSA.
- Compare predictions of our completed equilibrium model for PSA with experimental results obtained at CRDEC in a collaborative effort, if it is desired to do so. For a true test, it is necessary to have appropriate adsorption equilibrium relations and physical and thermodynamic parameters.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None. A copy of the M.S. thesis of Ronald K. King is being delivered to Dr. David Tevault with this report.

Blank

Quarterly Report #4

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: D.A.A15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: July 9, 1991

Period Covered: March 13, 1991 – June 12, 1991

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of hydrocarbon vapors.

Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the co-adsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the period covered by the previous quarterly report we completed the measurement of water adsorption/desorption isotherms on Calgon Type BPL activated carbon. Isotherms were measured at 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.

Our first two hydrocarbons chosen for study were n-hexane and acetone. We have a considerable amount of pure component isotherm data on these substances. Hexane is essentially immiscible with water while acetone is completely miscible.

During the present reporting period we completed the measurement of adsorption/desorption isotherms for n-hexane/water and acetone/water coadsorbed on BPL activated carbon at 25°C and 100°C. The hysteresis loops for water were found to persist, were more pronounced

for the n-hexane/water system than for the acetone/water system, and closed with increasing temperature. Very importantly, the presence of adsorbed water was found to increase significantly the partial pressure of the adsorbed hydrocarbon, with this behavior being more pronounced for the n-hexane/water system.

Our research on adsorption equilibria completed to date under the contract is described in the Ph.D. dissertation of Edgar N. Rudisill, who completed his dissertation and received his degree in May, 1991. A copy of the dissertation was delivered to Dr. David Tevault on May 29, 1991.

Discussions were held at CRDEC on March 21 and 22 on compounds to be considered next. Our previous intention was to consider hexanol next because of its partial miscibility with water. However, the discussion indicated that it may be more advantageous for us to consider instead chlorofluorocarbon-type compounds, choosing them on the basis of volatility, water solubility, and molecular size. Two of the simulants used at CRDEC currently fall into this classification (CFC-113 and perfluorocyclobutane).

Following the discussions, we developed the following list of candidate compounds. The compounds are available as refrigerants, blowing agents, cleaning agents, and aerosol propellants. Our intention is to measure pure component isotherms and isotherms with water coadsorption for selected compounds on the list. We will appreciate further discussions with CRDEC personnel in paring down the list and possibly adding other, more interesting compounds.

- One Carbon Atom

- CFC-12 CCl_2F_2
- HCFC-22 CHClF_2
- Dichloromethane CH_2Cl_2

- Two Carbon Atoms

- CFC-113 $\text{CCl}_2\text{FCClF}_2$
- HFC-134a $\text{CF}_3\text{CH}_2\text{F}$
- HCFC-123 CHCl_2CF_3
- HCFC-141b $\text{CH}_3\text{CCl}_2\text{F}$
- HFC-125 CHF_2CF_3

- HCFC-124 CHClFCF_3
- HFC-152a CH_3CHF_2
- HFC-152 $\text{CH}_2\text{FCH}_2\text{F}$
- HCFC-142b CH_3CClF_2

- Many Carbon Atoms

- Perfluorocyclobutane
- 1.1.2.2.3.4 Hexafluoro-3.4 bis-(trifluoromethyl)cyclobutane

We have purchased CFC-113 and dichloromethane to begin our studies. These were chosen in part because both compounds are liquids at room temperature and our apparatus is currently set up to handle liquid injections. We are now completing the calibration of our apparatus and beginning experiments with CFC-113.

PSA Model

We have begun the construction of a robust, generic mathematical model for PSA as described in our previous quarterly reports. Initially, we have constructing an *equilibrium* model. We have written computer code to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL. This work is described in detail in the Masters of Science thesis of Ronald K. King. A copy of the thesis was delivered to Dr. David Tevault with the previous quarterly report.

The initiation of the development of our fixed-bed *rate* model was mentioned in the previous quarterly report. This reporting period we have continued the development of the rate model for PSA. We are basing the model on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) of King. Our purpose in doing so is to reduce the computer time necessary to run the model. One change in the equation set is that a momentum balance is

no longer included; instead, at any time the pressure in the bed is assumed to be uniform. We expect the model to be as flexible and as easy to use as that of King.

As part of the rate model we are including intraparticle convection effects. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps. It can also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection during pressurization and blowdown changes the initial condition of the bed for those steps.

As part of the PSA modeling, we have recently begun to examine mathematical methods for converging directly on the periodic states (cyclic steady states) of adsorption cycles. The traditional approach has been to run cycles repeatedly until the periodic state is reached. Such an approach can be very slow. We expect that our methods will be able to find the periodic state in much less computer time. We intend to build the capability of directly converging on periodic states into our rate model.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on March 21 - 22 and May 29 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- Continue to measure adsorption equilibria for vapors of organic compounds. Both pure component adsorption and coadsorption with water vapor will be considered.
- Continue to plan future work with other compounds.

PSA Model

- Continue our recently initiated work on the fixed-bed rate model for PSA.
- Compare predictions of our completed equilibrium model for PSA with experimental results obtained at CRDEC in a collaborative effort, if it is desired to do so. For a true test, it is necessary to have appropriate adsorption equilibrium relations and physical and thermodynamic parameters.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Quarterly Report #5

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAA-A15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: October 7, 1991

Period Covered: June 13, 1991 - September 12, 1991

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of hydrocarbon vapors.

Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the co-adsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms have been measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Adsorption/desorption isotherms for n-hexane/water and acetone/water coadsorbed on BPL activated carbon have been measured at 25°C and 100°C. (n-Hexane and acetone were the first two hydrocarbons chosen for coadsorption with water because we had previously measured pure component isotherms for these substances [at 25°C,

50°C, 75°C, 100°C, and 125°C] and because hexane is essentially immiscible with water while acetone is completely miscible.) The hysteresis loops for water were found to persist, were more pronounced for the n-hexane/water system than for the acetone/water system, and closed with increasing temperature. Very importantly, the presence of adsorbed water was found to increase significantly the partial pressure of the adsorbed hydrocarbon, with this behavior being more pronounced for the n-hexane/water system.

- Additional compounds have been identified for detailed study. A list of such compounds resulted from discussions held at CRDEC on March 21 - 22, 1991 and is contained in the previous quarterly report. The discussion indicated we should consider some chlorofluorocarbon-type compounds, choosing them on the basis of volatility, water solubility, and molecular size. Two of the simulants used at CRDEC currently fall into this classification (CFC-113 and perfluorocyclobutane). Our intention is to measure pure component isotherms and isotherms with water coadsorption for selected compounds on the list. We will appreciate further discussions with CRDEC personnel in identifying other interesting compounds with different functionalities.

During the present reporting period we accomplished the following:

- Isotherms were measured for CFC-113 (CCl_2FCClF_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation. A graph of these data is appended to this report.
- We began the measurement of isotherms for dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Type BPL carbon over a range of temperatures.

PSA Model

We have begun the construction of robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructing an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption

and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.

- Our work on the development of a fixed-bed *rate* model was mentioned in the previous two quarterly reports. This reporting period we continued the development of the rate model which we are basing on an explicit equation set $(dy/dt = \dots)$ where y is the dependent variable vector rather than on the implicit equation set $(A dy/dt = \dots)$ where A is a matrix used in the equilibrium model. Our purpose in doing so is to reduce the computer time necessary to run the model. We are including both intraparticle diffusion and convection effects in the rate model. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps. It can also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection during pressurization and blowdown changes the initial condition of the bed for those steps.
- We continued to examine mathematical methods for converging directly on the periodic states (cyclic steady states) of PSA cycles, as mentioned in the previous quarterly report. The traditional approach has been to run cycles repeatedly until the periodic state is reached. Such an approach can be very slow. We expect that our methods will be able to find the periodic state in much less computer time. We intend to build the capability of directly converging on periodic states into our rate model. This reporting period we presented a brief report on this work at the NSF-CNRS Workshop on Adsorption Processes for Gas Separation in Gif sur Yvette, France.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC. Aberdeen Proving Ground on July 11 - 12 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We will continue to measure adsorption equilibria for vapors of organic compounds. Both pure component adsorption and coadsorption with water vapor will be considered. Specifically, for the next reporting period, we expect to complete the measurement of isotherms for dichloromethane adsorbed on Type BPL carbon. Also, we will measure adsorption/desorption isotherms for the coadsorption of CFC-113/water and dichloromethane/water, although it is not likely that we will complete this phase of the work until the following reporting period.
- We will continue discussions with CRDEC personnel to plan future work with other compounds.

PSA Model

- We will continue our work on the fixed-bed rate model for PSA. We are including both intraparticle diffusion and convection (during pressurization and blowdown) in the model. Also, as part of this effort, we will continue to investigate the direct determination of periodic states of adsorption cycles.

- We will compare predictions of our completed equilibrium model for PSA with experimental results obtained at CRDEC in a collaborative effort, if it is desired to do so. For a true test, it is necessary to have appropriate adsorption equilibrium relations and physical and thermodynamic parameters.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

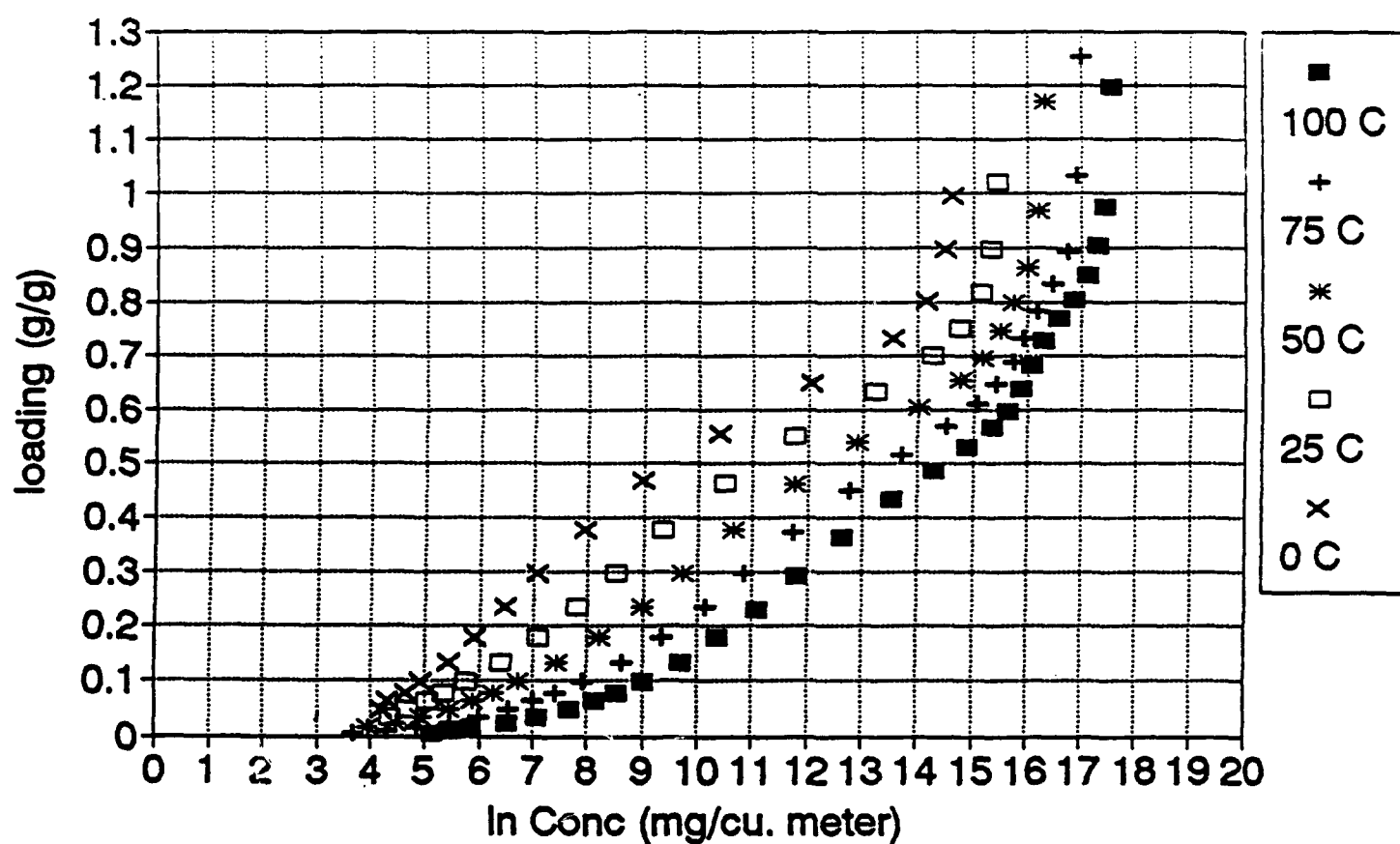
804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

A graph of recently measured data for CFC-113 adsorbed on Calgon Type BPL activated carbon is shown on the following page.

Adsorption Isotherms

1, 1, 2 trichloro-1, 2, 2 trifluoroethane



Blank

Quarterly Report #6

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: December 16, 1991

Period Covered: September 13, 1991 – December 12, 1991

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of vapors or organic compounds.

Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms have been measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Adsorption/desorption isotherms for n-hexane/water and acetone/water coadsorbed on BPL activated carbon have been measured at 25°C and 100°C. (n-Hexane and acetone were the first two hydrocarbons chosen for coadsorption with water because we had previously measured pure component isotherms for these substances at 25°C,

50°C, 75°C, 100°C, and 125°C and because hexane is essentially immiscible with water while acetone is completely miscible.) The hysteresis loops for water were found to persist, were more pronounced for the n-hexane/water system than for the acetone/water system, and closed with increasing temperature. Very importantly, the presence of adsorbed water was found to increase significantly the partial pressure of the adsorbed hydrocarbon, with this behavior being more pronounced for the n-hexane/water system.

- Additional compounds have been identified for detailed study. A list of such compounds resulted from discussions held at CRDEC on March 21 - 22, 1991 and is contained in a previous quarterly report. The discussion indicated we should consider some chlorofluorocarbon-type compounds, choosing them on the basis of volatility, water solubility, and molecular size. Continued discussions with CRDEC personnel will help us to identify other interesting compounds with different functionalities.
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation.
- We began the measurement of isotherms for dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Type BPL carbon over a range of temperatures.

During the present reporting period we accomplished the following:

- We completed measurement of isotherms for dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Type BPL carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation.
- We measured adsorption equilibria for water and CFC-113 (CCl_2FCClF_2) coadsorbed on Calgon Type BPL activated carbon at 25°C and 100°C.
- We presented a paper entitled "Multicomponent Adsorption Equilibria for Vapors of Hydrocarbons and Water on Activated Carbon" at the U.S. Army Scientific Conference held at Aberdeen Proving Ground in November, 1991. This paper described much of our work under the contract.
- A paper entitled "Coadsorption of Hydrocarbons and Water on BPL Activated Carbon" was cleared by the U. S. Army CRDEC for publication in a refereed journal.

- Two additional graduate students joined LeVan's group to carry out research on the adsorption equilibria aspects of this contract. Three graduate students are now working on adsorption equilibrium (with one graduating soon). Two other students are currently working on the PSA fixed-bed processes.

PSA Model

We are constructing robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.
- Our work on the development of a fixed-bed *rate* model was mentioned in previous quarterly reports. This reporting period we continued the development of the rate model which we are basing on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. Our purpose in doing so is to reduce the computer time necessary to run the model. We are including both intraparticle diffusion and *convection* effects in the rate model. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps, such as those used with weakly adsorbed light gases. It can also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection

during pressurization and blowdown changes the initial condition of the bed for those steps.

This reporting period we made significant progress on the rate model. Convection was implemented successfully at the particle scale. Our effort is now on implementing the rate model at the bed level. We expect to have completed the development of an isothermal model incorporating both diffusion and convection effects by the end of the next reporting period. The development of a nonisothermal model will follow the completion of the isothermal model.

- We continued to examine mathematical methods for converging directly on the periodic states (cyclic steady states) of PSA cycles, as mentioned in the previous quarterly report. The traditional approach has been to run cycles repeatedly until the periodic state is reached. Such an approach can be very slow. We expect that our methods will be able to find the periodic state in much less computer time. We intend to build the capability of directly converging on periodic states into our rate model.

We continue to make good, normal progress in this area.

- Discussions were held at CRDEC on October 17 and 18, 1991, on modeling efforts at CRDEC and the University of Virginia. Specifically, we discussed at what points it would be desirable to build into the CRDEC model features that had been and were being developed at the University of Virginia. Some aspects that may be built into the CRDEC model in the near future in a collaborative effort are (i) the ability to converge directly on periodic states, and (ii) the ability to treat thermal effects encountered during pressurization and blowdown steps.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on October 17 - 18, 1991 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We will measure adsorption equilibria for dichloromethane (methylene chloride, CH_2Cl_2) and water coadsorbed on Type BPL carbon at 25°C and 100°C.
- We have recently identified the possibility that a slight amount of hysteresis exists in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We intend to perform a few short experiments to check this possibility. There is precedent in the literature for a slight amount of hysteresis for hydrocarbons adsorbed on activated carbons at high relative pressures.
- We will continue discussions with CRDEC personnel to plan future work with other compounds. We believe that the coadsorption of some *light gases with water* should be considered. For these, water can be expected to have a dramatic effect. Also, in recent discussions at CRDEC, studies of coadsorption of organic vapors has been suggested. Coadsorption of *mixed organic vapors of compounds differing greatly in volatility* has not been studied to any significant degree (if at all) and should be very interesting. Such systems in vapor-liquid equilibrium provide challenging tests for predictive models.
- We will move our apparatus into the new Chemical Engineering Building now under construction and nearing completion at the University of Virginia. The apparatus will be set back up and experiments begun with other compounds. Depending on what

compounds are considered (e.g., light gases), modifications to the apparatus may be necessary.

- We will continue to work toward a truly predictive model for coadsorption of water and organics on activated carbon. We recognize that more data, especially involving light gases coadsorbed with water, will be necessary for comprehensive understanding.

PSA Model

- We will continue our work on the fixed-bed rate model for PSA. We are including both intraparticle diffusion and convection in the model as described above. The completion of a isothermal model is expected during the next reporting period.
- We will continue to investigate the direct determination of periodic states of adsorption cycles. This work looks very promising.
- If desired at this time, we will collaborate in the development of a mathematical model to predict the PSA experimental results obtained at CRDEC. We can help to implement thermal effects during pressurization and blowdown, the direct determination of periodic states, and other things.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

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Quarterly Report #7

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: March 20, 1992

Period Covered: December 13, 1991 - March 12, 1992

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of vapors of organic compounds. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms have been measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Adsorption/desorption isotherms for n-hexane/water and acetone/water coadsorbed on BPL activated carbon have been measured at 25°C and 100°C. (n-Hexane and acetone were the first two hydrocarbons chosen for coadsorption with water because we had previously measured pure component isotherms for these substances at 25°C, 50°C, 75°C, 100°C, and 125°C and because hexane is essentially immiscible with water

while acetone is completely miscible.) The hysteresis loops for water were found to persist, were more pronounced for the n-hexane/water system than for the acetone/water system, and closed with increasing temperature. Very importantly, the presence of adsorbed water was found to increase significantly the partial pressure of the adsorbed hydrocarbon, with this behavior being more pronounced for the n-hexane/water system.

- Additional compounds have been identified for detailed study. A list of such compounds resulted from discussions held at CRDEC on March 21 - 22, 1991 and is contained in a previous quarterly report. The discussion indicated we should consider some chlorofluorocarbon-type compounds, choosing them on the basis of volatility, water solubility, and molecular size. Continued discussions with CRDEC personnel will help us to identify other interesting compounds with different functionalities.
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation.
- Isotherms were measured for dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Type BPL carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation.
- Isotherms were measured for water and CFC-113 (CCl_2FCClF_2) coadsorbed on Calgon Type BPL activated carbon at 25°C and 100°C.

During the present reporting period we accomplished the following:

- Isotherms were measured for water and dichloromethane (methylene chloride, CH_2Cl_2) coadsorbed on Calgon Type BPL activated carbon at 25°C. Attempts to measure similar isotherms at 100°C showed that dichloromethane was very reactive in our apparatus at this temperature with water present.
- We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$), a possibility mentioned in the previous quarterly report. We did this by performing an experiment with CFC-113 at 50°C.
- We correlated the data of Rudisill for adsorption and desorption branches of water on BPL carbon at several temperatures using the Kelvin equation with a temperature dependent contact angle.

- Roy Eissmann completed and defended his M.S. thesis on CFC-113 and dichloromethane adsorption, separately and with water, and correlation of Rudisill's water data. Eissmann's analysis of data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicates a very strong dependence of quantity of water adsorbed on water solubility in the organic compound. A preliminary copy of this thesis is being forwarded to Dr. Tevault with this quarterly report. A final, corrected copy will be sent as soon as it is received from the binder.
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are as based on correct physical structure (to the extent possible).
- Discussions at CRDEC in January, 1992 indicated the need to consider lighter compounds coadsorbed with water. We had believed that the coadsorption of some *light gases with water* should be considered. For these, water can be expected to have a dramatic effect. Also, in recent discussions at CRDEC, studies of coadsorption of organic vapors has been suggested. Coadsorption of *mixed organic vapors of compounds differing greatly in volatility* has not been studied to any significant degree (if at all) and should be very interesting. Such systems in vapor-liquid equilibrium provide challenging tests for predictive models. Further discussions are indicated. It is hoped that these can be held in the very near future.
- We ordered and received a necessary new part (a pressure transducer multiplexer) to modify our apparatus to consider the adsorption of light gases, separately and in combination with water or heavy hydrocarbons.
- We disassembled our adsorption equilibrium apparatus in preparation to move it to the new Chemical Engineering Building at the University of Virginia. (The apparatus was moved on March 16, 1992.)

PSA Model

We are constructing robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of

which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.

- Our work on the development of a fixed-bed *rate* model was mentioned in previous quarterly reports. This reporting period we continued the development of the rate model which we are basing on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. Our purpose in doing so is to reduce the computer time necessary to run the model. We are including both intraparticle diffusion and *convection* effects in the rate model. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with *short cycle steps*, such as those used with *weakly adsorbed light gases*. It can also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection during pressurization and blowdown changes the initial condition of the bed for those steps.

This reporting period we discovered a significant simplification in the way to write and solve rate models for isothermal PSA. Previous models in which bed pressure was allowed to vary in time but not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed; this is done by integrating the balance over the length of the bed. This reporting period, we began to implement this method in our isothermal, intraparticle convection model for PSA beds.

- This quarter, in work related to the contract, M. D. LeVan began to develop a PSA

simulation model to analyze the CFC-113 PSA data gathered to date at CRDEC. The model includes an energy balance, as thermal effects during pressurization and blowdown have been found to be significant. The model uses the newly discovered way of treating the dP/dt derivative mentioned above.

- We continued to examine mathematical methods for converging directly on the periodic states (cyclic steady states) of PSA cycles, as mentioned in the previous quarterly report. The traditional approach has been to run cycles repeatedly until the periodic state is reached. Such an approach can be very slow. We expect that our methods will be able to find the periodic state in much less computer time.

This quarter we used our methods to analyze published claims that have been made by Farooq, Hassan, and Ruthven and by Ritter and Yang for the existence of multiple periodic states in PSA. We duplicated their PSA models and found that the multiple periodic states do not exist: only single periodic states were found for all cases.

- We continue to discuss the complementary and collaborative modeling efforts occurring at CRDEC and the University of Virginia. Some aspects developed at the University of Virginia that may be built into the CRDEC model in the future are (i) the ability to converge directly on periodic states, (ii) the ability to treat thermal effects encountered during pressurization and blowdown steps, (iii) the new way to handle the dP/dt derivative, and (iv) intraparticle convection effects.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on January 23 - 24, 1992 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We will move and reassemble our apparatus in the new Chemical Engineering Building.
- We will modify the apparatus to measure adsorption isotherms of light gases adsorbed separately and with water or heavy hydrocarbons. We will then begin to measure these isotherms.
- We will continue our effort on developing reliable, predictive, adsorption equilibrium models for organic compounds coadsorbed with water. We recognize that more data, especially involving light gases coadsorbed with water, will be necessary for comprehensive understanding.

PSA Model

- We will continue our work on the fixed-bed rate model for PSA. We are including both intraparticle diffusion and convection in the model as described above. The completion of the isothermal model is expected during the next reporting period.
- M. D. LeVan will continue his development of a PSA model to simulate the CFC-113 data gathered to date at CRDEC. Collaboration with U.S. Army and GEO-CENTERS personnel will be necessary. Completion of this model is expected by mid-May, 1992.
- We will continue to investigate the direct determination of periodic states of adsorption cycles. The method affords the possibility of mapping out solution spaces and determining optimal operating conditions easily.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Quarterly Report #8

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: D.A.A15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: July 17, 1992

Period Covered: March 13, 1992 – June 12, 1992

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of vapors of organic compounds. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms have been measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Adsorption/desorption isotherms for n-hexane/water and acetone/water coadsorbed on BPL activated carbon have been measured at 25°C and 100°C. (n-Hexane and acetone were the first two hydrocarbons chosen for coadsorption with water because we had previously measured pure component isotherms for these substances at 25°C, 50°C, 75°C, 100°C, and 125°C and because hexane is essentially immiscible with water

while acetone is completely miscible.) The hysteresis loops for water were found to persist, were more pronounced for the n-hexane/water system than for the acetone/water system, and closed with increasing temperature. Very importantly, the presence of adsorbed water was found to increase significantly the partial pressure of the adsorbed hydrocarbon, with this behavior being more pronounced for the n-hexane/water system.

- Isotherms were measured for CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation. We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We did this by performing an experiment with CFC-113 at 50°C.
- Isotherms were measured for water and CFC-113 coadsorbed at 25°C and 100°C and for dichloromethane coadsorbed on Calgon Type BPL activated carbon at 25°C. Attempts to measure similar isotherms at 100°C for dichloromethane at showed that dichloromethane was very reactive in our apparatus at this temperature with water present.
- We have found that data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicates a very strong dependence of quantity of water adsorbed on water solubility in the organic compound.
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are based on correct physical structure (to the extent possible).
- Additional compounds have been identified for detailed study. A list of such compounds resulted from discussions held at CRDEC in March, 1991 and is contained in the quarterly report covering that period. The discussion indicated we should choose compounds on the basis of volatility, water solubility, and molecular size. Discussions at CRDEC in January, 1992 indicated the need to consider some lighter gases coadsorbed with water. Also, in recent discussions at CRDEC, studies of coadsorption of organic vapors has been suggested. Coadsorption of mixed organic vapors of compounds differing greatly in volatility has not been studied to any significant degree

and should be very interesting. Such systems in vapor-liquid equilibrium provide challenging tests for predictive models. Continued discussions with CRDEC personnel will help us to identify other interesting compounds with different functionalities.

During the present reporting period we accomplished the following:

- The M.S. thesis of Eissmann on coadsorption of CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) with water on Calgon Type BPL activated carbon was finalized and a bound copy was delivered to Dr. Tevault.
- We moved our adsorption equilibrium apparatus to the new Chemical Engineering Building at the University of Virginia.
- We began modification of our adsorption equilibrium apparatus to measure adsorption equilibrium for coadsorption of light gases and water. This is a fairly major modification of the injection system of the apparatus. We installed equipment to allow us to measure quantities of gases injected into our closed loop.
- We continued our development of correlations and interpretations of the data of Rudisill for adsorption and desorption branches of water on BPL carbon at several temperatures. In addition to using the Kelvin equation with a temperature dependent contact angle, mentioned in the previous quarterly report, we are pursuing several other approaches.

PSA Model

We are constructing robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed,

and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.

- This reporting period we continued the development of our fixed-bed *rate* model which we are basing on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. Our purpose in doing so is to reduce the computer time necessary to run the model. We are including both intraparticle diffusion and *convection* effects in the rate model. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with *short cycle steps*, such as those used with *weakly adsorbed light gases*. It can also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection during pressurization and blowdown changes the initial condition of the bed for those steps. As part of the development of this model, we discovered a significant simplification in the way to write and solve rate models for isothermal PSA (and, approximately, for non-isothermal PSA). Previous models in which bed pressure was allowed to vary in time but not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed; this is done by integrating the balance over the length of the bed. This model is very near completion.
- This quarter, in work related to the contract, M. D. LeVan continued to develop PSA simulation models (isothermal and non-isothermal) to analyze the CFC-113 PSA data gathered to date at CRDEC. The models uses the newly discovered way of treating the dP/dt derivative mentioned above. Thus, pressurization and blowdown steps are treated by these models.
- This quarter, tests of the non-isothermal model described immediately above were conducted at CRDEC on April 30 and May 1, 1992. This model includes an energy balance, as thermal effects during pressurization and blowdown are believed to be significant. The model was not predicting the large temperature changes found in the

experiments. The model was checked, and then the interpretation of the experimental results became suspect. Additional experiments with glass beads, dry gases, etc. showed that the model was working correctly and that the temperature excursions found in the experiments were caused by coadsorption of light gases.

- We continued to examine mathematical methods for converging directly on the periodic states (cyclic steady states) of PSA cycles, as mentioned in the previous quarterly report. The traditional approach has been to run cycles repeatedly until the periodic state is reached. Such an approach can be very slow. We expect that our methods will be able to find the periodic state in much less computer time. We have used our methods to analyze published claims that have been made by Farooq, Hassan, and Ruthven and by Ritter and Yang for the existence of multiple periodic states in PSA. We duplicated their PSA models and found that the multiple periodic states do not exist: only single periodic states that are approached very slowly were found for all cases.
- We continue to discuss the complementary and collaborative modeling efforts occurring at CRDEC and the University of Virginia. Some aspects developed at the University of Virginia that may be built into the CRDEC model in the future are (i) the ability to converge directly on periodic states, (ii) the ability to treat thermal effects in PSA, (iii) the new way to handle the dP/dt derivative, and (iv) intraparticle convection effects.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

David K. Friday visited the University of Virginia on April 8, 1992 for research discussions.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on April 30 and May 1, 1992 for research discussions.

Shortly following this quarter, David E. Tevault visited the University of Virginia on June 15, 1992 for research discussions. New compounds were identified for further study of adsorption equilibrium.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We will complete modification of our apparatus to measure adsorption isotherms of gases adsorbed separately and with water. We will then begin to measure these isotherms. Compounds identified for study are propane, either ethane or n-butane, and CFC-12. We are beginning with propane.
- We intend to measure nitrogen adsorption and desorption isotherms on BPL carbon using a BET apparatus in our laboratory. This should contribute to our understanding of BPL carbon.
- We will continue our effort on developing reliable, predictive, adsorption equilibrium models for organic compounds coadsorbed with water. We recognize that more data, especially involving light gases coadsorbed with water, will be necessary for comprehensive understanding.

PSA Model

- We will continue our work on fixed-bed rate models for PSA. The isothermal model, which includes both intraparticle diffusion and convection effects as described above, will be finalized.
- M. D. LeVan will continue his development of PSA models to simulate the CFC-113 data gathered to date at CRDEC. Coadsorption of nitrogen must be included in the non-isothermal model. Collaboration with U.S. Army and GEO-CENTERS personnel will be necessary.

- We will continue to investigate the direct determination of periodic states of adsorption cycles. The method affords the possibility of mapping out solution spaces and determining optimal operating conditions easily.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Quarterly Report #9

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: September 28, 1992

Period Covered: June 13, 1992 – September 12, 1992

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of vapors of organic compounds. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms were measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation. We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We did

this by performing an experiment with CFC-113 at 50°C.

- Adsorption/desorption isotherms for n-hexane/water, acetone/water, and CFC-113/water coadsorbed on BPL activated carbon were measured at 25°C and 100°C. (Prior to the start of the contract we had measured pure component isotherms for hexane and acetone on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C.) Isotherms for dichloromethane/water were measured at 25°C; attempts to measure similar isotherms at 100°C showed that dichloromethane was very reactive in our apparatus at this temperature with water present.
 - The hysteresis loops for water were found to persist with coadsorption of the hydrocarbon or halocarbon and closed with increasing temperature.
 - The presence of adsorbed water was found to increase the partial pressure of the adsorbed organic compound. with the extent of this increase depending on the system and being more pronounced for n-hexane/water than acetone/water.
 - We have found that data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicates a very strong dependence of quantity of water adsorbed on water solubility in the organic compound.
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are based on correct physical structure (to the extent possible).
- Additional compounds have been identified for detailed study through discussions with CRDEC personnel. These are contained in previous quarterly reports. The discussions have indicated we should choose compounds on the basis of volatility, water solubility, and molecular size. Discussions at CRDEC in January, 1992 indicated the need to consider some lighter gases coadsorbed with water. Also, in recent discussions at CRDEC, studies of coadsorption of organic vapors has been suggested. Coadsorption of mixed organic vapors of compounds differing greatly in volatility has not been studied to any significant degree and should be very interesting. Such systems in vapor-liquid equilibrium provide challenging tests for predictive models. Continued discussions with CRDEC personnel will help us to identify other interesting compounds with different functionalities.
- We moved our adsorption equilibrium apparatus to the new Chemical Engineering

Building at the University of Virginia and began modification to measure adsorption equilibrium for coadsorption of light gases and water. This is a fairly major change of the injection system of the apparatus. We installed equipment to allow us to measure quantities of gases injected into our closed loop.

During the present reporting period we accomplished the following:

- We completed modification of our adsorption equilibrium apparatus to measure adsorption equilibrium for coadsorption of light gases and water. The measurement system was calibrated. We began and are close to completion of measurement of pure component isotherms of propane adsorbed on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C.
- We measured nitrogen adsorption and desorption isotherms on our BPL carbon using a BET apparatus in our laboratory. This contributes to our understanding of BPL carbon.
- We began determining isosteric heats of adsorption directly from our data for the components on which we have comprehensive adsorption equilibrium data. The behavior of isosteric heat of adsorption with loading gives us qualitative information on heterogeneity of the adsorbent and adsorption mechanism.
- We continued our development of correlations and interpretations of the data on BPL carbon for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We are pursuing several approaches, ranging from largely physical interpretations to purely mathematical descriptions.
- We continued to discuss the complementary and collaborative efforts occurring at CRDEC and the University of Virginia on measurement, interpretation, and correlation of adsorption equilibrium.

PSA Model

We are constructing robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of

which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.

- This reporting period we completed the initial development of our fixed-bed *rate* model. This work is described in an M.S. thesis, a copy of which will be delivered to CRDEC when received. The model is based on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. This was done to reduce the computer time necessary to run the model.
 - We included both intraparticle diffusion and *convection* effects in the rate model. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with *short cycle steps*, such as those used with *weakly adsorbed light gases*. It may also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection during pressurization and blowdown can change the initial condition of the bed for those steps.
 - As part of the development of this model, we discovered a significant simplification in the way to write and solve rate models for isothermal PSA (and, approximately, for non-isothermal PSA). Previous models in which bed pressure was allowed to vary in time out not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed; this is done by integrating the balance over the length of the bed.

- In work related to the contract, M. D. LeVan continued to develop PSA simulation models (isothermal and non-isothermal) and dispersion models to analyze data gathered at CRDEC. The PSA models use the newly discovered way of treating the dP/dt derivative mentioned above. Thus, pressurization and blowdown steps are treated by these models. Tests of these models have been conducted at CRDEC and continued development is occurring jointly. Recently, John J. Mahle has modified the non-isothermal PSA model to try to predict the large temperature changes found in the PSA experiments for CFC-113. A computer program for a new type of dispersion model was developed by M. D. LeVan at CRDEC in August following discussions with David K. Friday.
- We continued to examine mathematical methods for converging directly on the periodic states (cyclic steady states) of PSA cycles, as mentioned in previous quarterly reports. The traditional approach has been to run cycles repeatedly until the periodic state is reached. Such an approach can be very slow. We expect that our methods will be able to find the periodic state in much less computer time.
 - We have used our methods to analyze published claims that have been made by Farooq, Hassan, and Ruthven and by Ritter and Yang for the existence of multiple periodic states in PSA. We duplicated their PSA models and found that the multiple periodic states do not exist; only single periodic states that are approached very slowly were found for all cases.
 - We have begun to investigate ways to converge directly on a periodic state that meets a desired product specification.
- We continue to discuss the complementary and collaborative modeling efforts occurring at CRDEC and the University of Virginia on fixed bed modeling. Some aspects developed at the University of Virginia that may be built into the CRDEC model in the future are (i) the ability to converge directly on periodic states, (ii) the ability to treat thermal effects in PSA, (iii) the new way to handle the dP/dt derivative, and (iv) intraparticle convection effects.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

David E. Tevault visited the University of Virginia on June 15, 1992 for research discussions. New compounds were identified for further study of adsorption equilibrium: these are propane, either ethane or n-butane, and CFC-12.

M. D. LeVan visited CRDEC, Aberdeen Proving Ground on July 23 and 24, 1992 and August 10 to 12, 1992 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We will complete measurement of adsorption isotherms for propane and begin, perhaps complete, measurement of propane/water isotherms.
- We will complete our analysis of isosteric heats of adsorption obtained directly from our existing data.
- We will continue our effort to develop reliable, predictive, adsorption equilibrium models and correlational methods for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We recognize that more data, especially involving light gases coadsorbed with water, will be necessary for comprehensive understanding.

PSA Model

- We will continue our work on fixed-bed rate models for PSA. Enhancements to existing models are planned and new models are under consideration. Non-isothermal effects should be added to our rate model.
- M. D. LeVan will continue his development of models to analyze data gathered at CRDEC. Collaboration with U.S. Army and GEO-CENTERS personnel will be necessary.
- We will continue to investigate the direct determination of periodic states of adsorption cycles. The method affords the possibility of mapping out solution spaces and determining optimal operating conditions easily.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Quarterly Report #10

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: December 23, 1992

Period Covered: September 13, 1992 – December 12, 1992

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of vapors of organic compounds. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms were measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation. We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We did

this by performing an experiment with CFC-113 at 50°C.

- Adsorption/desorption isotherms for n-hexane/water, acetone/water, and CFC-113/water coadsorbed on BPL activated carbon were measured at 25°C and 100°C. (Prior to the start of the contract we had measured pure component isotherms for hexane and acetone on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C.) Isotherms for dichloromethane/water were measured at 25°C; attempts to measure similar isotherms at 100°C showed that dichloromethane was very reactive in our apparatus at this temperature with water present. Our data show the following:
 - The hysteresis loops for water were found to persist with coadsorption of the hydrocarbon or halocarbon and closed with increasing temperature.
 - The presence of adsorbed water was found to increase the partial pressure of the adsorbed organic compound, with the extent of this increase depending on the system and being more pronounced for n-hexane/water than acetone/water.
 - We have found that data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicates a very strong dependence of quantity of water adsorbed on water solubility in the organic compound.
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are based on correct physical structure (to the extent possible).
- Additional compounds have been identified for detailed study through discussions with ERDEC personnel. These are contained in previous quarterly reports. The discussions have indicated we should choose compounds on the basis of volatility, water solubility, and molecular size. Discussions at ERDEC (January, 1992) have indicated the need to consider some lighter gases coadsorbed with water. In the most recent discussions (June, 1992) of compounds, propane, either ethane or n-butane, and CFC-12 were identified for study. Also, studies of coadsorption of mixed organic vapors of compounds differing greatly in volatility has been suggested; these have not been studied to any significant degree and should be both interesting and a challenging test for predictive models. Continued discussions with ERDEC personnel will help us to identify other interesting compounds.

- We modified and calibrated our adsorption equilibrium apparatus to measure adsorption equilibrium for coadsorption of light gases and water. This is a major change of the injection system of the apparatus.
- We measured nitrogen adsorption and desorption isotherms on our BPL carbon using a BET apparatus in our laboratory. This contributes to our understanding of BPL carbon.

During the present reporting period we accomplished the following:

- We measured pure component isotherms of propane adsorbed on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C. We are currently reproducing this data.
- We ran tests to confirm that nitrogen carrier gas at 0.1 MPa does not compete to any measurably degree with propane for the adsorption space in BPL carbon. These tests were performed by substituting helium for nitrogen. No differences in propane loading as a function of propane pressures were found.
- We completed the determination of isosteric heats of adsorption directly from our data for the components on which we have comprehensive adsorption equilibrium data. The behavior of isosteric heat of adsorption with loading gives us qualitative information on heterogeneity of the adsorbent and adsorption mechanism.
- We continued our development of correlations and interpretations of the data on BPL carbon for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We are pursuing several related approaches, ranging from largely physical interpretations to purely mathematical descriptions. Some details on our developments are as follows:
 - We have begun to develop methods that we believe should guarantee the accurate correlation of adsorption equilibrium data. The methods are based on the use of series expansions in terms of polynomials that are orthogonal to summation, although non-orthogonal polynomials could also be used. In implementing the method, a multicomponent, temperature-dependent virial-type equation arises naturally. We have applied this method to only limited data to date, but the initial results are very encouraging.
 - We have applied mean-field density-functional theory to determine the pore size distribution of BPL activated carbon using a nitrogen isotherm at 78 K that we

measured. This method gave a pore size distribution that agreed remarkably well with the pore size distribution that we obtained using the Kelvin equation and water desorption isotherms measured previously by Rudisill under the contract. This is a confirmation of nanometer scale structural information for BPL activated carbon.

- We have begun to develop a semi-empirical model to describe the adsorption of pure gases and vapors in microporous adsorbents in general, and the adsorption of water vapor and pure organic compounds on BPL activated carbon in particular. The model assumes that the adsorbate molecules are localized on the adsorbent surface. Allowance is made for multilayer formation and pore filling as the pressure is increased. The heterogeneity of the adsorbent surface and lateral interactions among adsorbate molecules are also accounted for in a simple fashion. Preliminary results indicate that the model predicts reasonably well our experimental adsorption isotherms for n-hexane, n-octane, acetone, dichloromethane, CFC-113, and water on BPL activated carbon over broad ranges of temperature and pressure.
- We are attempting to extending the pure component isotherm equations referred to immediately above to adsorption of mixed vapors of organic compounds and water. Our isotherm equations predict experimental adsorption isotherms reasonably well for much of our organic/water data, but we have found that much better agreement can be obtained by introducing a binary adsorbate-adsorbate interaction parameter.
- We designed a new apparatus to measure pure gas isotherms for light organic compounds and their mixtures with water vapor. The apparatus is described in detail in a proposal recently submitted to ERDEC. We believe that the apparatus will give improved performance over our existing apparatus when applied to light adsorbates. The apparatus is housed in an environmental chamber and can be operated in two different modes. First, for measurement of pure isotherms, gas is injected into a closed loop using a gas injection system and is recirculated until equilibrium is established, as determined and measured with a gas chromatograph. Second, for measurement of mixture isotherms of the organic compound and water, the apparatus is initially used in a flow-through mode to saturate the adsorbent at a chosen relative humidity. This is a major change from our existing apparatus, which attempts to fix adsorbed rather

than vapor concentrations. During the flow-through step, the environmental chamber is slowly cooled or heated to put the components on an adsorption or desorption branch of the isotherm. After the bed is saturated as desired, the apparatus is reconfigured in a closed loop and heated with circulation to remove the adsorbates, which are collected in a liquid nitrogen trap for later analysis by pressure and gas chromatograph measurements after expansion back to vapor.

- We continued to discuss the complementary and collaborative efforts occurring at ERDEC and the University of Virginia on measurement, interpretation, and correlation of adsorption equilibrium.

PSA Model

We are constructing robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.
- This reporting period we made modifications to our fixed-bed *rate* model and studied its behavior for a wide range of operating conditions. The model is based on an explicit equation set ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. This was done to reduce the computer time necessary to run the model.
 - We included both intraparticle diffusion and convection effects in the rate model. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and

purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps, such as those used with weakly adsorbed light gases. It may also be important for processes with long feed and purge steps if intraparticle diffusion is the controlling mass transfer resistance because convection during pressurization and blowdown can change the initial condition of the bed for those steps.

- As part of the development of this model, we discovered a significant simplification in the way to write and solve rate models for isothermal PSA (and, approximately, for non-isothermal PSA). Previous models in which bed pressure was allowed to vary in time but not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed: this is done by integrating the balance over the length of the bed.
- In work related to the contract, M. D. LeVan continued to develop PSA simulation models (isothermal and non-isothermal) and dispersion models to analyze data gathered at ERDEC. The PSA models use the newly discovered way of treating the dP/dt derivative mentioned above. Thus, pressurization and blowdown steps are treated by these models. Tests of these models have been conducted at ERDEC and continued development is occurring jointly. Recently, John J. Mahle has modified the non-isothermal PSA model to try to predict the large temperature changes found in the PSA experiments for CFC-113.
- Also, in work related to the contract, a computer program for a new type of dispersion model was developed by M. D. LeVan at ERDEC in August following discussions with David K. Friday. This reporting period we continued discussions of the model, in particular how to allow pressure to change with time.
- We continue to discuss the complementary and collaborative modeling efforts occurring at ERDEC and the University of Virginia on fixed bed modeling.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited ERDEC on October 19 and 20, 1992 for research discussions.

M. D. LeVan presented a paper authored by Roy N. Eissmann, entitled "Vapor-Phase Adsorption Equilibria of Halocarbon - Water Mixtures on Activated Carbon," at the ERDEC Scientific Conference on November 19, 1992.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We will continue our measurements of adsorption isotherms for pure light organic compounds and their mixtures with water vapor on BPL activated carbon.
- We will continue our effort to develop reliable, predictive, adsorption equilibrium models and correlational methods for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We recognize that more data, especially involving light gases coadsorbed with water, will be necessary for comprehensive understanding.

PSA Model

- We will continue our work on fixed-bed rate models for PSA. Enhancements to existing models are planned and new models are under consideration.

- M. D. LeVan will continue his development of models to analyze data gathered at ERDEC. Collaboration with U.S. Army and GEO-CENTERS personnel will be necessary.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.

Blank

Quarterly Report #11

Contractor's Name and Address:

University of Virginia
School of Engineering and Applied Science
Department of Chemical Engineering
Thornton Hall
Charlottesville, VA 22903-2442

Contract Number: DAAA15-90-C-0012

Nomenclature of the System or Program:

Improved Filtration Materials and Modeling

Date of Report: March 23, 1993

Period Covered: December 13, 1992 – March 12, 1993

Title of Report:

Contractor's Progress, Status & Management Report
Quarterly Progress Report

CDRL Sequence Number: A001

Security Classification: Unclassified

Name of Issuing Government Activity: US ARMY AMCCOM

The lettering of sections below corresponds to that in the contract in paragraphs 10.3 of the preparation instructions for this report.

A. Front cover sheet.

See previous page.

B. Description of progress made against milestones during reporting period.

The contract contains two tasks: (1) the measurement and interpretation of single and multicomponent adsorption equilibria, and (2) the construction and testing of a generic mathematical model for pressure swing adsorption (PSA) incorporating the adsorption isotherms and including rate phenomena and thermal effects. These tasks are considered separately below.

Adsorption equilibria

The research involves the adsorption of water and other compounds on activated carbon. Our goals are to establish a comprehensive understanding of water adsorbed by itself on activated carbon, and following this to consider the adsorption of other components separately and in combination with water. We will determine the effects of water vapor on the adsorption of vapors of organic compounds. Water is known to exhibit a pronounced hysteresis loop when adsorbed as a pure component on activated carbon at room temperature. It will be important in the PSA model to know how this loop affects and is affected by the coadsorption of other compounds. Our approach is to measure water isotherms not only at room temperature, but at conditions well removed from room temperature. This will permit more accurate correlation of the isotherm data as well as the extraction of reliable thermal properties from the data for use in the PSA model.

During the periods covered by previous quarterly reports, we have completed the following:

- Water adsorption/desorption isotherms were measured on Calgon Type BPL activated carbon at temperatures of 25°C, 50°C, 75°C, 100°C, and 125°C for water pressures from low values to saturation. The hysteresis loop was found to close and shift toward the right on a typical isotherm plot as the adsorption temperature increased.
- Isotherms were measured for CFC-113 (CCl_2FCClF_2) and dichloromethane (methylene chloride, CH_2Cl_2) adsorbed on Calgon Type BPL activated carbon at 0°C, 25°C, 50°C, 75°C, and 100°C from low pressures to saturation. We confirmed the existence of a slight amount of hysteresis in our pure component data for pure organic compounds adsorbed on BPL activated carbon at high relative pressures ($P/P_{sat} > 0.3$). We did

this by performing an experiment with CFC-113 at 50°C.

- Adsorption/desorption isotherms for n-hexane/water, acetone/water, and CFC-113/water coadsorbed on BPL activated carbon were measured at 25°C and 100°C. (Prior to the start of the contract we had measured pure component isotherms for hexane and acetone on BPL carbon at 25°C, 50°C, 75°C, 100°C, and 125°C.) Isotherms for dichloromethane/water were measured at 25°C; attempts to measure similar isotherms at 100°C showed that dichloromethane was very reactive in our apparatus at this temperature with water present. Our data show the following:
 - The hysteresis loops for water were found to persist with coadsorption of the hydrocarbon or halocarbon and closed with increasing temperature.
 - The presence of adsorbed water was found to increase the partial pressure of the adsorbed organic compound, with the extent of this increase depending on the system and being more pronounced for n-hexane/water than acetone/water.
 - We have found that data for coadsorption of hexane, acetone, CFC-113, and dichloromethane with water indicates a very strong dependence of quantity of water adsorbed on water solubility in the organic compound.
- We obtained scanning electron micrographs of our BPL carbon to help us in developing adsorption equilibrium and rate models that are based on correct physical structure (to the extent possible).
- Additional compounds have been identified for detailed study through discussions with ERDEC personnel. These are contained in previous quarterly reports. The discussions have indicated we should choose compounds on the basis of volatility, water solubility, and molecular size. Discussions at ERDEC (January, 1992) have indicated the need to consider some lighter gases coadsorbed with water. In the most recent discussions (June, 1992) of compounds, propane, either ethane or n-butane, and CFC-12 were identified for study. Also, studies of coadsorption of mixed organic vapors of compounds differing greatly in volatility has been suggested; these have not been studied to any significant degree and should be both interesting and a challenging test for predictive models. Continued discussions with ERDEC personnel will help us to identify other interesting compounds.

- We modified and calibrated our adsorption equilibrium apparatus to measure adsorption equilibrium for coadsorption of light gases and water. This is a major change of the injection system of the apparatus.
- We measured nitrogen adsorption and desorption isotherms on our BPL carbon using a BET apparatus in our laboratory. This contributes to our understanding of BPL carbon.
- We ran tests to confirm that nitrogen carrier gas at 0.1 MPa does not compete to any measurably degree with propane for the adsorption space in BPL carbon. These tests were performed by substituting helium for nitrogen. No differences in propane loading as a function of propane pressures were found.
- We determined isosteric heats of adsorption directly from our data for the components on which we have comprehensive adsorption equilibrium data. The behavior of isosteric heat of adsorption with loading gives us qualitative information on heterogeneity of the adsorbent and adsorption mechanism.
- We have applied mean-field density-functional theory to determine the pore size distribution of BPL activated carbon using a nitrogen isotherm at 78 K that we measured. This method gave a pore size distribution that agreed remarkably well with the pore size distribution that we obtained using the Kelvin equation and water desorption isotherms measured previously by Rudisill under the contract. This is a confirmation of nanometer scale structural information for BPL activated carbon.
- We designed a new apparatus to measure pure gas isotherms for light organic compounds and their mixtures with water vapor. The apparatus is described in detail in a proposal recently submitted to ERDEC. We believe that the apparatus will give improved performance over our existing apparatus when applied to light adsorbates. The apparatus is housed in an environmental chamber and can be operated in two different modes. First, for measurement of pure isotherms, gas is injected into a closed loop using a gas injection system and is recirculated until equilibrium is established, as determined and measured with a gas chromatograph. Second, for measurement of mixture isotherms of the organic compound and water, the apparatus is initially used in a flow-through mode to saturate the adsorbent at a chosen relative humidity. This is a major change from our existing apparatus, which attempts to fix adsorbed rather

than vapor concentrations. During the flow-through step, the environmental chamber is slowly cooled or heated to put the components on an adsorption or desorption branch of the isotherm. After the bed is saturated as desired, the apparatus is reconfigured in a closed loop and heated with circulation to remove the adsorbates, which are collected in a liquid nitrogen trap for later analysis by pressure and gas chromatograph measurements after expansion back to vapor.

During the present reporting period we accomplished the following:

- We remeasured pure component isotherms of propane adsorbed on BPL carbon at 25°C and 100°C. The data were measured with helium in the recirculation loop although, based on results discussed in the previous quarterly report, we could just as well have used nitrogen.
- We found it necessary this quarter to have magnets in the Ruska circulating pump remagnetized.
- We continued our development of correlations and interpretations of the data on BPL carbon for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We are pursuing several related approaches, ranging from largely physical interpretations to purely mathematical descriptions.
- We continued our development of methods that we believe should guarantee the accurate correlation of adsorption equilibrium data. The methods are based on the use of series expansions in terms of polynomials that are orthogonal to summation, although non-orthogonal polynomials could also be used. In implementing the method, a multicomponent, temperature-dependent virial-type equation arises naturally.
- In March, Brad Russell defended his M.S. thesis. A copy will be delivered to Dr. David Tevault as soon as it is received from the binder. Brad is now beginning his Ph.D. studies. Major components of Brad's M. S. thesis are
 - The scanning electron micrographs of BPL carbon referred to above.
 - The BET nitrogen adsorption and desorption isotherms measured on BPL carbon referred to above.

- The application of mean-field density-functional theory to determine the pore size distribution of BPL activated carbon using a nitrogen isotherm at 78 K as referred to above.
 - The determination of isosteric heats of adsorption directly from our data as referred to above.
 - The initial development of a semi-empirical model to describe the adsorption of pure gases and vapors in microporous adsorbents in general, and the adsorption of water vapor and pure organic compounds on BPL activated carbon in particular. The model assumes that the adsorbate molecules are localized on the adsorbent surface. Allowance is made for multilayer formation and pore filling as the pressure is increased. The heterogeneity of the adsorbent surface and lateral interactions among adsorbate molecules are also accounted for in a simple fashion.
 - Attempts to extend the pure component isotherm equations referred to immediately above to adsorption of mixed vapors of organic compounds and water. Our isotherm equations predict experimental adsorption isotherms reasonably well for much of our organic/water data, but we have found that much better agreement can be obtained by introducing a binary adsorbate-adsorbate interaction parameter.
- We continued to discuss the complementary and collaborative efforts occurring at ERDEC and the University of Virginia on measurement, interpretation, and correlation of adsorption equilibrium.

PSA Model

We are constructing robust, generic mathematical models for PSA as described in our previous quarterly reports. This work can be broken down as follows, with later models building on previous ones.

- Initially, we constructed an *equilibrium* model. Computer code was written to set up material balances for an arbitrary number of components, any number including all of which may be adsorbable. These were combined with an energy balance and an Euler equation-type momentum balance to treat pressure drop for various steps in the PSA cycle. The material balances and energy balances are coupled through heat effects associated with pressurization and blowdown and heat effects associated with adsorption and desorption. Four different types of boundary conditions are implemented for the

material and energy balances for the unpacked, mixing regions that exist at each end of the bed. These conditions are: constant molar flowrate, valve equation, pressure fixed, and end closed. The balances and boundary conditions were set up by orthogonal collocation on finite elements using the software package PDECOL.

- We have constructed fixed-bed *rate* models and studied their behavior for a wide range of operating conditions. The models are based on explicit equation sets ($dy/dt = \dots$ where y is the dependent variable vector) rather than on the implicit equation set ($A dy/dt = \dots$ where A is a matrix) used in the equilibrium model. This was done to reduce the computer time necessary to run the model.
 - We have included both intraparticle diffusion and convection effects in the rate models. During the pressurization and blowdown steps of PSA gas flows into and out of the adsorbent particles because of the large pressure change. During the feed and purge steps some convection continues as adsorption/desorption removes/adds molecules from/to the gas phase, thereby creating small pressure variations. Convection can be expected to be important for PSA processes operated with short cycle steps, such as those used with weakly adsorbed light gases.
 - As part of the development of these models, we discovered a significant simplification in the way to write and solve rate models for isothermal PSA (and, approximately, for non-isothermal PSA). Previous models in which bed pressure was allowed to vary in time but not distance have required the user to specify the pressure derivative dP/dt during pressurization and blowdown. We have found a way to calculate this derivative from an overall material balance, given the flowrates into and out of the bed; this is done by integrating the balance over the length of the bed.
- In work related to the contract, M. D. LeVan has developed PSA simulation models (isothermal and non-isothermal) and dispersion models to analyze data gathered at ERDEC. The PSA models use the newly discovered way of treating the dP/dt derivative mentioned above. Thus, pressurization and blowdown steps are treated by these models. Tests of these models have been conducted at ERDEC and continued development is occurring jointly. John J. Mahle has modified the non-isothermal PSA model to try to predict the large temperature changes found in the PSA experiments for CFC-113.

- Also, in work related to the contract, a computer program for a new type of dispersion model was developed by M. D. LeVan following discussions with Dr. David K. Friday.

During the present reporting period we accomplished the following:

- We continued the development of our fixed bed rate models with and without intra-particle convection.
- In conjunction with John Mahle, we continued to collaborate on the development of a reliable PSA model to analyze data gathered at ERDEC.
- We continued to discuss the complementary and collaborative modeling efforts occurring at ERDEC and the University of Virginia on fixed bed modeling.

C. Results, positive or negative, obtained related to previously identified problem areas, with conclusions and recommendations.

There are no previously identified problem areas.

D. Any significant changes to the contractor's organization or method of operation.

None.

E. Problem areas affecting technical or scheduling elements, with background and any recommendations for solutions beyond the scope of the contract.

None.

F., G., H., and I.

Do not apply.

J. Any trips and significant results.

M. D. LeVan visited ERDEC on January 14 and 15, 1993 for research discussions.

K. Record of all significant telephone calls and any commitments made by telephone.

None.

L.

Does not apply.

M. Contract schedule status.

The contract work is proceeding as planned. Progress is consistent with the contract schedule.

N. Plans for activities during the following reporting period.

Our plans for the following reporting period are as follows:

Adsorption equilibria

- We are setting up our adsorption equilibrium apparatus to measure organic/water adsorption equilibrium for n-octane and water on BPL activated carbon. We will then study propane and water. It is our feeling that data for propane and water will be more accurate if we have had the experience of considering a less volatile system first.
- We will continue our effort to develop reliable, predictive, adsorption equilibrium models and correlational methods for pure component adsorption/desorption of water, pure component adsorption of organic compounds, and mixed adsorption/desorption of organics/water. We recognize that more data, especially involving light gases coadsorbed with water, will be necessary for comprehensive understanding.

PSA Model

- We will continue our work on fixed-bed rate models for PSA.
- M. D. LeVan will continue his collaboration with U.S. Army on the development of models to analyze data gathered at ERDEC.

O. Name and telephone number of preparer or report.

M. Douglas LeVan

804/924-6279

P. Appendices for any necessary tables, references, photographs, illustrations, and charts.

None.